

**Final Report for the National Aeronautics and Space Administration
EOS Validation Program Award Number NAG5-9955**

“Stable Isotopes and Radiocarbon in Atmospheric Methane and its Sources”

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Beginning September 1, 2000 and continuing to November 30, 2001 we received funding from NASA contract NAG5-9955. We conducted research aimed at further understanding atmospheric methane (CH_4), carbon monoxide (CO), and non-methane (C1-C5) hydrocarbons (NMHCs). We made measurements of mixing ratios in atmospheric CH_4 , CO and NMHCs as well as measurements providing supporting data such as stable and radiocarbon isotope measurements in these trace gases to answer questions posed by their global distribution and changes in their mixing ratios in the atmosphere.

The research reported here is a both a continuation and expansion of our air sample collections, measurements, and analyses and interpretations of CH_4 and CO data collected from fixed land surface locations, from shipboard transects of the Pacific Ocean between Los Angeles, CA and Auckland, New Zealand, and from upper air samples (free troposphere to lower stratosphere) taken from aircraft. The mixing ratio data of CH_4 and CO at specific spatial and temporal coordinates can be compared to data obtained by the MOPITT (Measurement of Pollution in the Troposphere Experiment) instrument onboard the NASA satellite Terra, launched December 1999, thereby providing a measure of validation for satellite based observations of CH_4 and CO mixing ratios. For example, from shipboard transects we can report mixing ratio data at the earth's surface in locations not readily available for study by other sample platforms. The timing of our shipboard and aircraft air sample collections are subject to spatial and temporal constraints by the ship and/or aircraft mission schedules. However, many individual sample points coincide with the EOS Terra satellite positioning.

Our mixing ratio working reference gases for CH_4 and CO analyses are based on the NOAA/CMDL reference scale for these gases and have been inter-compared with and calibrated to NOAA/CMDL reference standards. Our level of precision for measurements of CH_4 and CO are $\sim\pm 5$ to 10 ppb for CH_4 (0.25-0.50% uncertainty around 1800 ppb) and $\sim\pm 3$ -5 ppb for CO (2.0 to 3.5% uncertainty around 145 ppb).

Our fixed surface sites are located at the mid-continental site Niwot Ridge, CO (41°N, 105°W) and at the coastal northern hemispheric site Montaña de Oro State Park, CA (35°N, 121°W). At these two sites we collect air samples approximately bi-monthly. The California site is close to a terminus of our trans-Pacific shipboard sampling transect running between Los Angeles, CA and Auckland, New Zealand (covering approximately 35°N to 35°S latitude and approximately 115°W and 176°E longitude). During 2000 and 2001 we made four shipboard sampling trips (June 2000, January 2001, September 2001, and December 2001). We also obtained upper air samples from NASA ER-2 flights during the SOLVE (Stratospheric Aerosol and Gas Experiment [SAGE] III Ozone Loss and Validation Experiment) campaign of January to March 2000.

Air samples are collected as grab samples at all locations. They are either collected into pre-treated aluminum cylinders using specially cleaned and modified Rix sweet air compressors (at Niwot Ridge, CO, and on board Blue Star container ships) or are collected into pre-treated

stainless steel canisters using oil-less, greaseless stainless steel bellows or piston pump/compressors (at Montaña de Oro, CA, on board Blue Star container ships, and from SOLVE aircraft campaign). No mixing or isotope ratio measurement instrumentation is utilized during these remote collections. Instead, all mixing ratio measurements are made using gas chromatography with flame ionization (CH_4) or reduction gas analyzer (CO) type detectors in our lab. All isotope ratio measurements are made using isotope ratio mass spectrometers in our lab. These measurement systems have been optimized to give the highest reported precisions and accuracies possible for CH_4 and CO trace gas species.

At Montaña de Oro and Niwot Ridge, we report two years of approximately bi-weekly measurement data during 2000-2001 including date and local time of collection. A few 2001 samples are still to be analyzed for both Montaña de Oro and Niwot Ridge. Figure 1 plots CH_4 mixing and isotope ratios versus date starting in 1996 through 2000 at Montaña de Oro as one example of how the fixed surface data is studied. Clear seasonal cycles in both CH_4 concentration and $^{13}\text{C}/^{12}\text{C}$ ratio are seen each year. The curve fit to the data is a least squares (2-harmonic) equation of the form

$$Y = A + B \times T + C \sin(T) + D \cos(T).$$

We have forced a seasonal cycle based on a 12 month year by holding $T = 2\pi \times \text{days}/365$. Other parameters are chosen by least squares method.

Of the four shipboard sampling transects of the tropical Pacific Ocean made since the launching of the Terra satellite, air samples from the first three have been completely measured. The total number of air samples collected on each trip of approximately 17 days, including multiple samples and sampling times for many dates, as follows: June 2000, 24; January 2001, 51; September 2001, 38; and December 2001, 38. Figure 2 shows the mixing and $^{13}\text{C}/^{12}\text{C}$ isotope ratio data of CH_4 for all cylinder air samples from the first three transects while Figure 3 shows the mixing ratio data for CO for the first three transects all plotted versus latitude. Of course, reported data for each sample collected for EOS validation includes latitude, longitude, and local time and well as measurement data.

In mid-2001, we analyzed air samples collected during NASA's SOLVE aircraft program through a collaboration with Elliott Atlas (National Center for Atmospheric Research) and Kristie Boering (Univ. of Calif. at Berkeley). The measurements we made are from air samples collected in the lower stratosphere during January through March 2000 at or near the South Pole and include measurement of CH_4 only. We will report this data to the EOS Validation program after conferring with our collaborators and adhering to data release rules for the SOLVE program.

Thus far, we have written two papers based on samples measurements and interpretation of data obtained during support from the EOS validation program. Two other papers are in preparation at present. These four papers are listed on the next page. We are in contact with EOS researchers at NCAR (Merritt Deeter and Louisa Emmons) and will be sending them several Excel spreadsheets with all pertinent data for Montaña de Oro, Niwot Ridge, and our Pacific Ocean transects soon. We will also send updated data through the end of the year as soon we have finished measurements of samples from our latest ship transect and late 2001 surface data.

Finally, our CH_4 and CO data from the samples described above are currently being used along with published data in other studies in a collaborative modeling study with Prof. Ivar Isaksen of the University of Oslo, Norway. The new 3-D GCM2 model from Oslo (which uses wind velocities, sub grid processes, temperatures, humidity and surface pressure data that has been extracted from the European Center for Medium range Weather Forecasting data base) is being used to explain the abrupt changes in CH_4 mixing ratio growth rate in the period from 1996-2000 and to study kinetic isotope effects in CH_4 loss processes such as CH_4 reaction with OH, Cl, $\text{O}(^1\text{D})$. Data of CO mixing ratios are incorporated into this new model to improve interactive calculations of CH_4 and CO sinks such as reaction with OH and $\text{O}(^1\text{D})$ (CH_4 only). A 3D model is needed to properly describe latitudinal mixing across the equator in particular and the effects of the uneven distribution of surface CH_4 sources and the soil sink both latitudinally and longitudinally.

Publications resulting from NASA contract NAG5-9955

Tyler, S. C., H. O. Ajie, A. L. Rice, E. C. Tuazon, and R. J. Cicerone, Experimentally determined kinetic isotope effects in the reaction of CH₄ with Cl: Implications for atmospheric CH₄, *Geophys. Res. Lett.*, 27, 1715-1718, 2000.

Rice, A. L., A. A. Gotoh, H. O. Ajie, and S. C. Tyler, High-precision continuous-flow measurement of ¹³C and D of atmospheric CH₄, *Anal. Chem.*, 73, 4104-4110, 2001.

Rice, A. L., S. C. Tyler, M. C. McCarthy, K. A. Boering, and E. Atlas, Measurements of the D/H and ¹³C/¹²C isotope ratios of stratospheric CH₄ from the POLARIS, STRAT, and SOLVE campaigns, in preparation for submission to *J. Geophys. Res.*

Tyler, S. C., H. O. Ajie, A. L. Rice, A. M. S. McMillan, R. J. Cicerone, and D. C. Lowe, Measurements of methane mixing ratio and ¹³C in air along a transect over the Pacific Ocean between Auckland, New Zealand and Los Angeles, California, in preparation for submission to *J. Geophys. Res.*

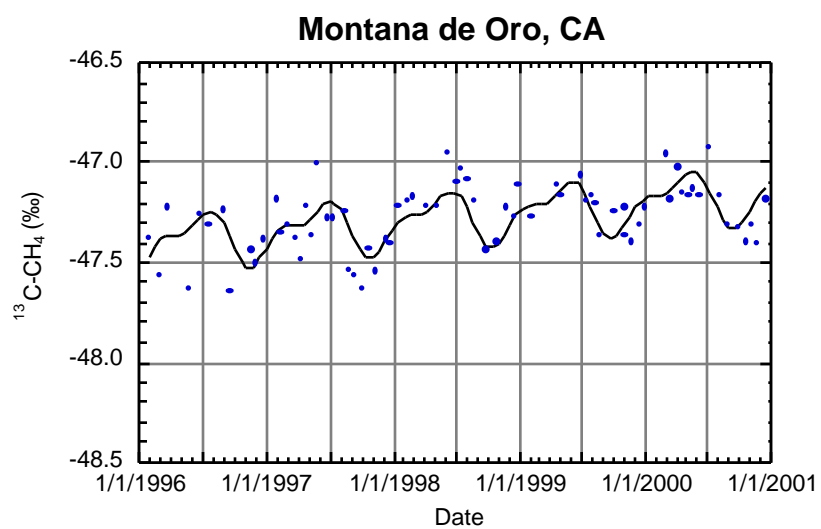


Fig. 1A

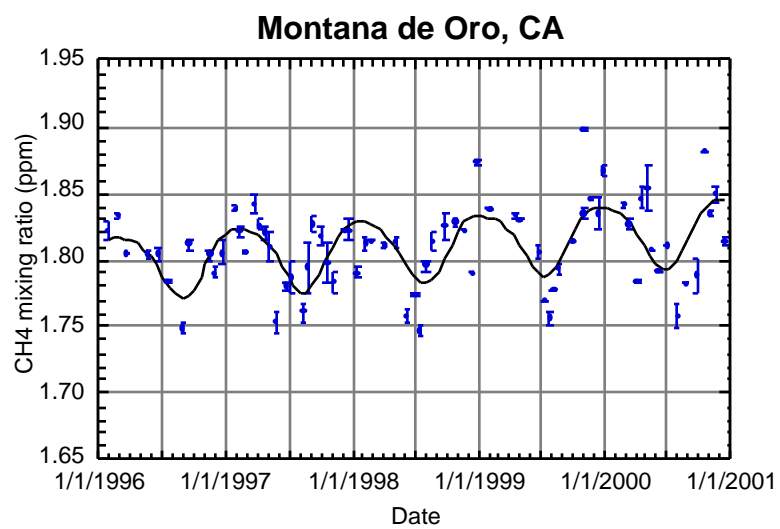


Fig. 1B

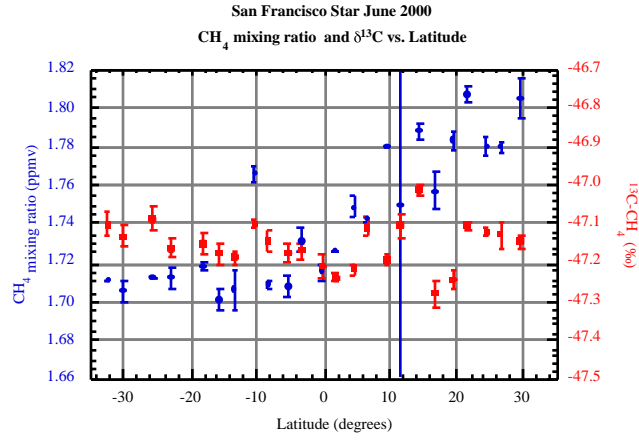


Fig. 2A

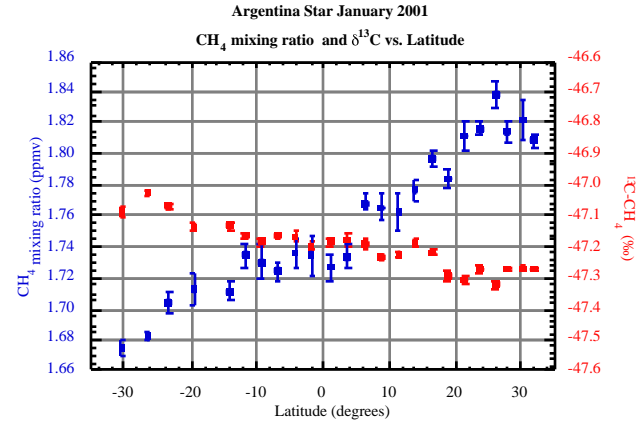


Fig. 2B

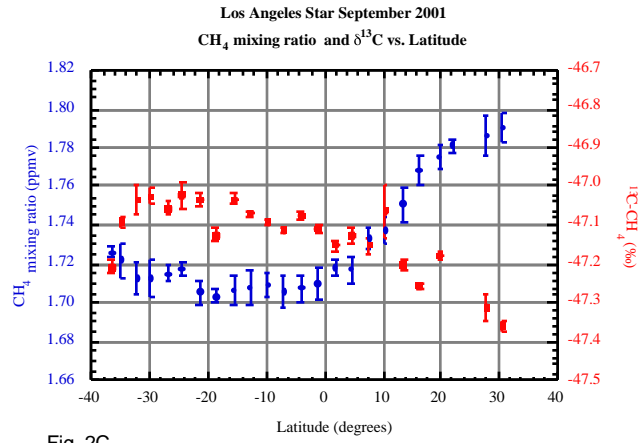


Fig. 2C

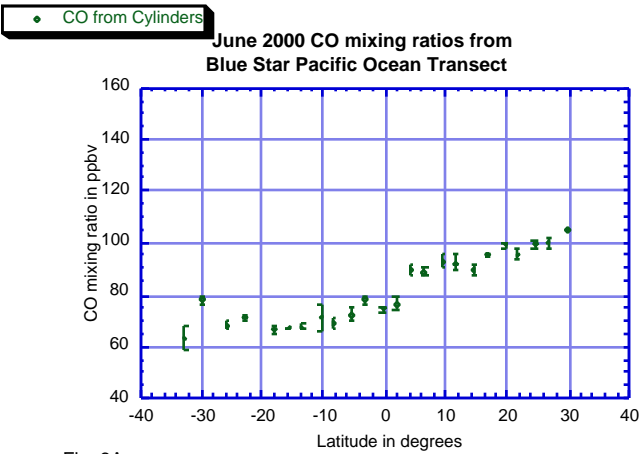


Fig. 3A

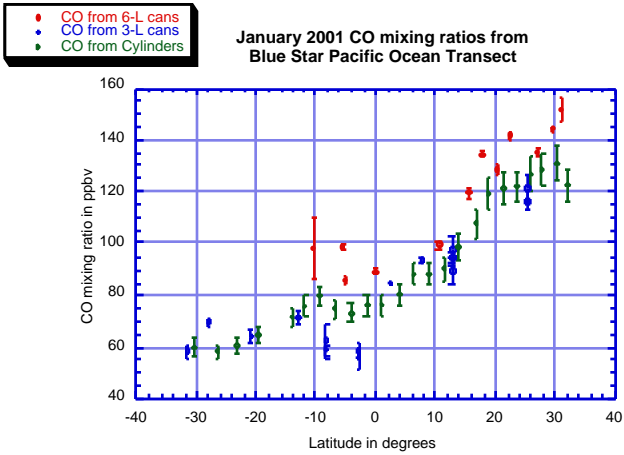


Fig. 3B

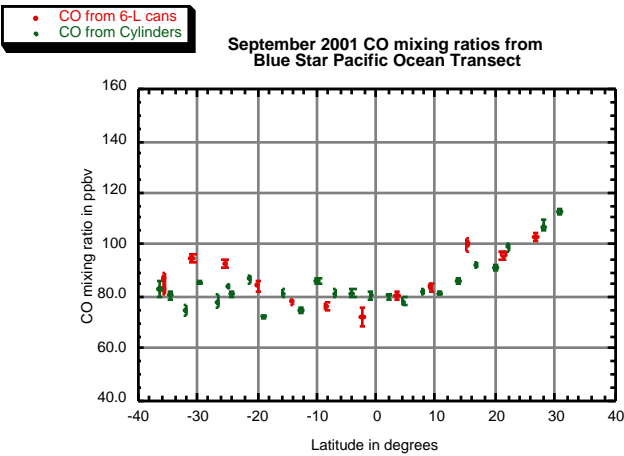


Fig. 3C